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TECHNICAL NOTE
D-108

RELATIONSHIP OF POLYMER STRUCTURE TO

THERMAL DETERIORATION OF ADHESIVE

BONDS IN METAL JOINTS

By J. M. Black and R. F. Blomquist

Forest Products Laboratory

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SUMMARY

Polymer structure of adhesives used to bond aluminum and stainless steel was correlated with their resistance to thermal deterioration when aged for 100 hours at temperatures up to 600° F.

The phenol-formaldehyde, polyamide, and butadiene-acrylonitrile polymers were the most resistant of the single resins used to bond aluminum. The polyamide and butadiene-acrylonitrile polymers were most resistant to thermal deterioration of the resins used to bond stainless steel.

Combinations of phenol resin with epoxy resins, polyamide, or butadiene copolymers; polyamide resins with epoxy resins or diallyl melamine; and epoxy resins with ethylacrylate-maleic anhydride copolymer had high thermal resistance in bonds on aluminum. In bonds to stainless steel, the most thermally stable polymer combinations were phenol resin with butadiene-acrylonitrile copolymer, epoxy resin with ethylacrylate-maleic anhydride copolymer, and polyamide resins combined with either epoxy resins, diallyl melamine, or butadiene copolymer and allyl glycidyl ether.

These results and observations indicated that an unsaturated carbon-to-carbon bond in a polymer promoted high resistance to thermal deterioration in bonds to stainless steel. Studies of crosslinking epoxy resins with polyamide and of vinyl copolymers with anhydride side groups indicated that when ester crosslinkages are presumably formed, thermal resistance, particularly in bonds to stainless steel, was much improved.

INTRODUCTION

Adhesive bonds to metal when subjected to elevated temperatures may undergo chemical deterioration that is irreversible. The course of this reaction depends upon the temperature, the kind of metal bonded, and the chemical structure of the adhesive and results in a permanent loss in strength of the bond.

In experimental work at this Laboratory for the Aeronautical Research Laboratory of the Wright Air Development Center (ref. 1), adhesive bonds to stainless steel with a phenol-epoxy type adhesive were low in resistance to thermal aging, while bonds to aluminum with the same adhesive were high in resistance. Some results of work, reference 2, on the relationship of metal surfaces to heat-aging properties of adhesive bonds also showed that thermal resistance of an adhesive bond was related to the chemical structure of the adhesive and of the metal adherent employed in the bond. Thus, for example, phenol-resin adhesives and phenol-epoxy adhesives showed no significant increases in deterioration for periods up to 200 hours at 550° F in bonds of aluminum but did show marked increases in deterioration in bonds on stainless steel. A straight epoxy-resin adhesive also deteriorated rapidly at 550° F in bonds on stainless steel. Bonds of a phenol-nitrile rubber adhesive were more resistant to thermal deterioration on stainless steel than on aluminum. A silicone adhesive was also greater in thermal resistance on stainless steel than on aluminum.

These observations suggest that specific chemical groups of a particular resin are more thermally stable than are other groups at elevated temperatures in the presence of a given metal and that the type of metal surface may have a specific effect on the thermal-aging properties of a given chemical group in the adhesive system.

The work reported here was directed toward further examination of the relationship of the chemical structure of the polymers to their thermal deterioration on metal surfaces at elevated temperatures and to the correlation of chemical structure with temperature and type of metal as a basis for a more fundamental approach to the formulation of a heat-resistant adhesive for the bonding of metals, such as stainless steel.

This investigation was conducted at the Forest Products Laboratory, U. S. Department of Agriculture under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

MATERIALS TESTED

Metals

Both 2024-T3 clad-aluminum alloy, 0.064 inch thick, and type 301 stainless steel, 1/2 hard and 0.020 inch thick, were bonded with each polymer investigated. Test specimens were prepared from these materials by bonding two 1- by 3.5-inch coupons into a lap-joint specimen with a 0.5-inch overlap. Preparation of individual specimens was done to eliminate the problem of bond failure or partial failure during cutting of specimens from a bonded panel. The thicknesses of the metals, 0.064 inch for aluminum and 0.020 inch for stainless steel, were selected to provide a test specimen for both metals that would have similar tensile properties. The aluminum, which was approximately three times greater in thickness than the steel, had a yield strength that was only about one-third of that of stainless steel - 44,000 pounds per square inch for aluminum and 125,000 pounds per square inch for stainless steel.

Polymers

A list of the polymers that were used in this experiment is shown in table 1. A total of 56 polymers, copolymers, and combinations were used as bonding agents for both metals. These polymers are designated by code numbers in the text and table 1 for convenience in reference. These materials were selected because of their desired chemical characteristics and not because of any known adhesive properties. Most of them had not been previously formulated as practical adhesives, and no attempts were made in this experiment to develop the most desirable adhesive formulations from them or to determine the optimum bonding conditions with each resin system. The resinous materials were applied to the metal surfaces as solutions, suspensions, or by hot-melt methods, whichever method seemed to be best suited for the material. When solvents were used in the application, they were removed before bonding by ovendrying the specimens for 30 minutes at 200° F. The information on methods of application, compositions of resin solutions, bonding temperatures and times, and bonding pressures is presented in table 1. Information on percentage compositions of polymers was obtained from the manufacturers. The resinous materials were employed without addition of curing agents or catalysts in order that the thermal-aging resistance of the polymers without modification could be obtained. Therefore some systems were definitely thermoplastic in nature. In all cases, the bonded specimens were removed from the press while hot and allowed to cool before further handling.

EXPERIMENTAL PROCEDURE

Preparation of Metal Surfaces for Bonding

Aluminum surfaces were prepared by wiping with methyl ethyl ketone and then by immersing the specimens for 5 minutes at 150° F in a solution of 10 grams of concentrated sulfuric acid, 1 gram of sodium dichromate, and 30 grams of water. The metal was then rinsed in cold tap water, distilled water, and was then air dried.

Stainless steel surfaces were prepared by wiping with methyl ethyl ketone and then immersing the specimens for 10 minutes at 150° F in a solution of 100 grams of concentrated hydrochloric acid, 4 grams of hydrogen peroxide (30 percent), 20 grams of formalin (40 percent), and 90 grams of water. The metal was rinsed with cold tap water and then immersed in the solution as used for the preparation of the aluminum surfaces.

These techniques of metal preparation had been found in previous work to be most suitable for adhesive bonding of such aluminum and stainless steel surfaces where heat aging was important.

Exposure and Test Conditions

Twenty-five individual lap-joint shear specimens with a 0.5-inch overlap were prepared for each adhesive and metal combination. After the initial bonding, 5 specimens were tested at 80° F and the remainder were subjected to aging in an oven at elevated temperatures. Specimens were removed from the oven and allowed to cool to room temperature before tests were begun. Five specimens for each condition were then tested after aging for 100 hours at 450°, 500°, 550°, and 600° F. Specimens were laid flat and carefully shimmed during heat aging to prevent premature failure due to thermoplastic flow of the adhesive. Since many of the polymeric materials investigated were known to be thermoplastic, the strength of bonds at the elevated temperatures was not determined. It was recognized that thermoplastic behavior would be unacceptable for adhesives for high-temperature service. It might be assumed, however, that if a polymer had very promising resistance to thermal deterioration and reasonably good adhesion, it could be formulated later with curing agents or modified by other means to reduce the thermoplastic behavior. The relative resistance of the bonds to thermal deterioration was determined from changes noted in the shear strength at 80° F after heat exposure.

The lap-joint shear specimens were loaded in tension in self-alining grips at the rate of 600 pounds per 0.5 square inch per minute until the adhesive bond failed in shear.

Temperatures during heat aging were controlled within ±3° F in special electrically heated ovens.
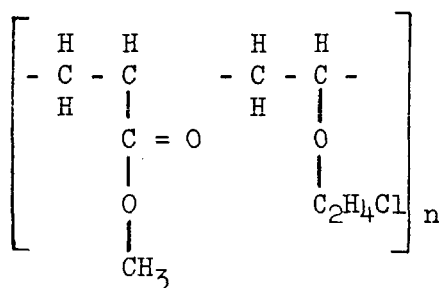
DISCUSSION

Joint Strength Tests

The results of all joint strength tests after aging of the specimens at the various temperatures for 100 hours are given in table 1. The methods of exposing and conditions for testing the various specimens are described in the preceding heading entitled "Exposure and Test Conditions." For convenience in reference and discussion, each different adhesive system is designated by a series number.

Adhesive Systems

The results for each adhesive composition are discussed separately in the following sections. The chemical composition and results of lap-joint tests for each series are shown in table 1.

Copolymer of methylacrylate and chloroethylvinylether (ser. 1).- Probable chemical structure:

$$
\begin{bmatrix}
\begin{array}{cccc}
\text{H} & \text{H} & \text{H} & \text{H} \\
-\text{C} - \text{C} & & -\text{C} - \text{C} - \\
\text{H} \quad | & & \text{H} \quad | \\
\text{C} = \text{O} & & \text{O} \\
| & & | \\
\text{O} & & \text{C}_2\text{H}_4\text{Cl} \\
| & & \\
\text{CH}_3 & &
\end{array}
\end{bmatrix}_n
$$

This copolymer made up of 95 percent of methylacrylate and 5 percent of chloroethylvinylether (C-1) showed evidence of crosslinking with itself with longer heating as the joint strength was increased after 100 hours of exposure at 450° and 500° F as compared to the unaged specimens. The strength of aluminum joints after aging at 450° and 500° F was significantly higher than that for stainless steel, even though the percentages of adhesion failure were not consistently higher on stainless steel.

The resin in about half of the joint areas in both types of bonds was deteriorated after 100 hours at 500° F without loss in joint strength compared to results at 450° and then was completely deteriorated after exposure at 550° F. This rather abrupt loss in thermal resistance may be directly related to the chlorine present in the polymer that could be released from the polymer in this temperature range and react with the metal surface to destroy the bond. Similar performance has been observed with commercially available neoprene-base adhesives at these temperatures. These result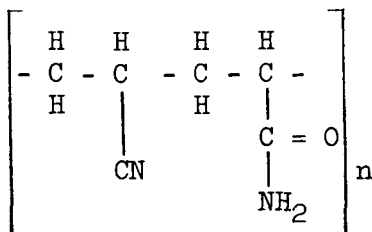s of thermal-aging tests on the copolymer suggest that resistance to deterioration would possibly be improved markedly by substitution of a more stable group for the chlorine group.

Polyacrylamide (ser. 2).- Probable chemical structure:

$$\begin{bmatrix} \begin{array}{cc} H & H \\ -C & -C- \\ H & | \\ & C=O \\ & | \\ & NH_2 \end{array} \end{bmatrix}_n$$
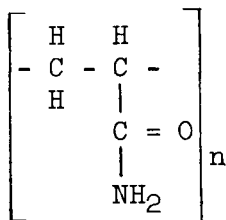
The polymer of acrylamide (PAA-1) with amide side groups as the reactive group showed no signs of crosslinking at elevated aging temperatures and was very low in thermal resistance. Joint strength was low in both aluminum and stainless steel bonds after aging the specimens 100 hours at 450° F or higher, with nearly complete charring in the joint areas, although initial strength was relatively high, particularly on steel. These results would indicate that amide side groups in a vinyl polymer were thermally unstable groups and were readily deteriorated.

Copolymer of acrylonitrile and acrylamide (ser. 3).- Probable chemical structure:

$$\begin{bmatrix} \begin{array}{cccc} H & H & H & H \\ -C & -C & -C & -C- \\ H & | & H & | \\ & | & & C=O \\ & CN & & | \\ & & & NH_2 \end{array} \end{bmatrix}_n$$

This copolymer (C-2) which contains both 25 percent of acrylamide and 75 percent of acrylonitrile was significantly lower in initial strength than the polyacrylamide of series 2. Resistance to thermal deterioration was essentially zero in this copolymer with complete charring in

joint areas, indicating that nitrile groups reduced adhesion to the metal surfaces and did not contribute to improved thermal resistance.

Copolymer of ethylacrylate and methacrylamide (ser. 4).- Probable chemical structure:

$$
\begin{bmatrix}
& & & & & & CH_3 \\
H & & H & & & H & | \\
-C & - & C & & -C & - & C- \\
H & & | & & H & & | \\
& & C=O & & & & C=O \\
& & | & & & & | \\
& & O & & & & NH_2 \\
& & | & & & & \\
& & C_2H_5 & & & &
\end{bmatrix}_n
$$
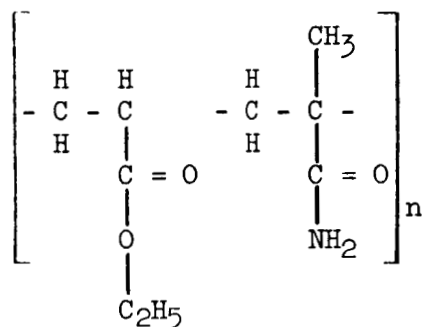
The formulation containing 95 percent of ethylacrylate and 5 percent of methacrylamide (C-3) provided further evidence in this group of data that amide side groups on the polymer were low in thermal stability. When compared with the results obtained with a similar copolymer in series 1 with chloroethylvinylether, the amide group appeared to lower thermal resistance and the tendency toward crosslinkage. There was also some indication in these tests that the ethylacrylate component of the copolymer was contributing to improved thermal stability in bonds to aluminum as evidenced by the relatively uniform but low joint strength after aging at the different temperatures.

Polyethylacrylate (ser. 5).- Probable chemical structure:

$$
\begin{bmatrix}
H & & H \\
-C & - & C- \\
H & & C=O \\
& & | \\
& & O \\
& & | \\
& & C_2H_5
\end{bmatrix}_n
$$
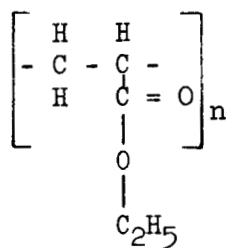
The results obtained with polyethylacrylate (PEA-1) revealed very little tendency of the ethyl ester group to crosslink but showed a reasonably high resistance to thermal deterioration of bonds on aluminum. Bonds of stainless steel were lower in strength with greater percentages of areas with charred adhesive at higher aging temperatures.

Copolymer of ethylacrylate and maleic anhydride (ser. 6).- Probable chemical structure:

$$
\begin{bmatrix}
\begin{array}{c}
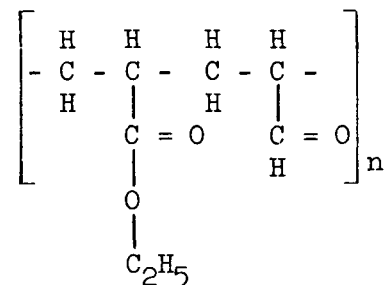\text{H} \quad \text{H} \qquad\quad \text{H} \quad \text{H} \\
-\text{C}-\text{C}- \quad - \quad \text{C}-\text{C}- \\
\quad\; | \qquad\qquad\quad | \quad\; | \\
\text{H} \quad \text{C}=\text{O} \qquad\; | \quad\; | \\
\qquad\; | \qquad\; \text{O}=\text{C}\quad\text{C}=\text{O} \\
\qquad \text{O} \qquad\qquad \text{O} \\
\qquad\; | \\
\qquad \text{C}_2\text{H}_5
\end{array}
\end{bmatrix}_n
$$
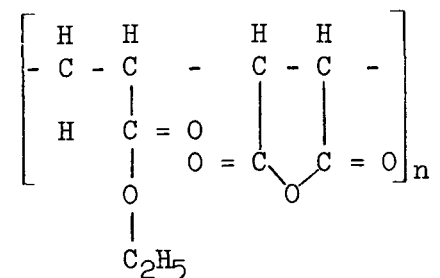
This copolymer (C-4), formed from 95 percent of ethylacrylate and 5 percent of maleic anhydride, showed similar performance in bonds to aluminum and stainless steel. It was lower in thermal resistance in bonds on aluminum than the polyethylacrylate of series 5, especially at 600° F.

Copolymer of ethylacrylate and acrolein (ser. 7).- Probable chemical structure:

$$
\begin{bmatrix}
\begin{array}{c}
\text{H} \quad \text{H} \quad\; \text{H} \quad \text{H} \\
-\text{C}-\text{C}-\text{C}-\text{C}- \\
\text{H} \quad\; | \quad\; \text{H} \quad\; | \\
\qquad \text{C}=\text{O} \qquad \text{C}=\text{O} \\
\qquad\; | \qquad\qquad \text{H} \\
\qquad \text{O} \\
\qquad\; | \\
\qquad \text{C}_2\text{H}_5
\end{array}
\end{bmatrix}_n
$$

The aldehyde side group in this copolymer (C-5) of 97.5 percent of ethylacrylate and 2.5 percent acrolein may have accounted for some cross-linking of the resin, since the joint strength increased after aging of the specimens at 450° and 500° F. Thermal deterioration of the polymer was quite apparent after aging at 550° F, and no marked difference was apparent from results on the 2 metal surfaces.

Copolymer of ethylacrylate and acrylonitrile (ser. 8).- Probable chemical structure:

$$
\begin{bmatrix}
\begin{array}{cccc}
H & H & H & H \\
-\,C & -\,C\,- & C & -\,C\,- \\
H & | & H & | \\
 & C=O & & | \\
 & | & & | \\
 & O & & CN \\
 & | & & \\
 & C_2H_5 & &
\end{array}
\end{bmatrix}_n
$$
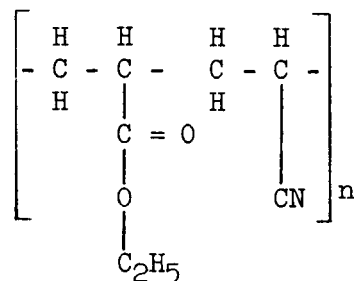
This copolymer (C-6), which consists of 95 percent of ethylacrylate and 5 percent of acrylonitrile showed very little further crosslinkage as aging temperature was increased. The amount of discoloration in the bond area was increased significantly at 500° F without appreciable change in joint strength. There was, however, a marked loss in strength when the specimens were aged at 550° F and 100 percent discoloration occurred in the bonded area on both metals. Properties were quite similar to other copolymers high in ethylacrylate.

Copolymer of ethylacrylate and acrylonitrile (ser. 9).- The chemical structure is the same as for series 8. The initial strength of copolymer bonds that consisted of 75 percent of ethylacrylate and 25 percent of acrylonitrile (C-7) to both aluminum and stainless steel were significantly higher than that of the 95:5 copolymer of series 8, showing the good crosslinking potential of the acrylonitrile component of the polymer. Bonds on both metals were deteriorated to a marked degree after 100 hours at 500° F with results considerably lower on aluminum at 600° F than in series 8, indicating that the increased acrylonitrile probably contributed to lower thermal resistance.

Copolymer of ethylacrylate and acrylonitrile (ser. 10).- The chemical structure is the same as for series 8. The initial strength of this copolymer (C-8) of 50 percent ethylacrylate and 50 percent acrylonitrile on aluminum and particularly on stainless steel was exceptionally high, indicating a greater degree of crosslinkage than was obtained with either the 95:5 or 75:25 copolymers of series 8 and 9. Resistance to thermal deterioration was low at 450° F, showing that the increased acrylonitrile content resulted in lower resistance to thermal deterioration as was also observed in bonds made with the 75:25 copolymer in series 9.

Copolymer of ethylacrylate and acrylonitrile (ser. 11).- The chemical structure is the same as for series 8. The initial strength of copolymer (C-9) that consisted of 15 percent of ethylacrylate and 85 percent of

acrylonitrile was much lower than that of the bonds made with 50:50 copoly-
mer of series 10, particularly on aluminum. These bonds had no resistance
to aging at 450° F on either metal. Further evidence thus was shown that
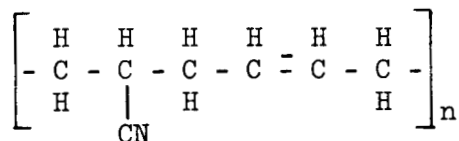acrylonitrile groups reduced thermal-aging resistance.

Polyacrylonitrile (ser. 12).- Probable chemical structure:

$$\left[\begin{array}{ccc} H & H & \\ -C & -C & - \\ H & | & \\ & CN & \end{array} \right]_n$$
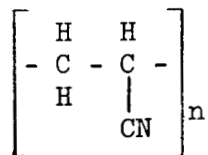
Polyacrylonitrile (PAN-1) showed no adhesion to either aluminum or stain-
less steel.

Copolymer of acrylonitrile and butadiene (ser. 13).- Probable chemical
structure:

$$\left[\begin{array}{cccccc} H & H & H & H & H & H \\ -C & -C & -C & -C & = C & -C - \\ H & | & H & & & H \\ & CN & & & & \end{array} \right]_n$$

This copolymer (C-10) of 35 percent of acrylonitrile with 65 percent of
butadiene (buna-N rubber) exhibited a significantly higher resistance to
thermal deterioration at 550° F than any other copolymers of acrylonitrile
with either ethylacrylate of series 8 to 12 or acrylamide of series 3.
A significant degree of crosslinkage also occurred in this copolymer as
joint strength was increased over the strength obtained after the initial
cure by aging at 500° and 550° F. This crosslinkage very likely occurred
through the unsaturated groups in the butadiene. The high resistance to
thermal deterioration in bonds to stainless steel also suggests that the
reactive unsaturated group in butadiene may either resist the catalytic
influences of the steel or react with some of the metal ions in the steel
to reduce their adverse catalytic effects through the formation of a
stable metallo-organic complex.

Copolymer of acrylonitrile and butadiene (ser. 14).- The chemical
structure is the same as for series 13. This copolymer of 25 percent
of acrylonitrile and 75 percent butadiene (C-11), with a slightly greater
amount of butadiene than the one described in series 13, showed even a
greater degree of crosslinkage and resistance to deterioration on long
heat aging than did the resins in series 13. The shear strength of
stainless steel bonds in series 14 was over 700 pounds per square inch
after aging the specimens for 100 hours at 600° F, and bonds to steel

were generally superior in strength at all temperatures to bonds to aluminum. These data were further evidence of a possibly strong thermally stable link between the unsaturated group in the butadiene component of the polymer and the metal components of stainless steel.

<u>Polyvinyl alcohol (ser. 15)</u>.- Probable chemical structure:

$$
\left[\begin{array}{cc} H & H \\ -\ C & -\ C\ - \\ H & | \\ & OH \end{array}\right]_n
$$
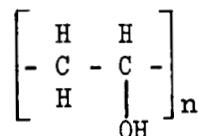
This polyvinyl alcohol polymer (PVA-1) showed very little initial strength and no resistance to aging at temperatures of 450° F and above.

<u>Phenol-formaldehyde resin (ser. 16)</u>.- Probable chemical structure:

$$
\left[\begin{array}{c} H \\ O \\ \\ H\qquad\qquad H \\ -\ C\ -\ \bigcirc\ -\ C\ - \\ H\qquad\qquad H \\ \\ H\ C\ H \\ | \\ OH \end{array}\right]_n
$$
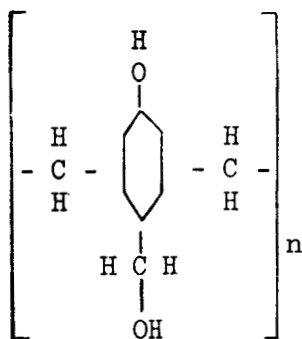
This phenol-formaldehyde resin (P-1), reported to be a 1-step resol type, had excellent resistance to thermal deterioration on aluminum at all conditions including 100 hours of aging at 600° F. The results obtained with this phenol resin demonstrate the high thermal stability that can be attained with aromatic structures such as are present in the phenol-formaldehyde condensation products. For purposes of comparison, the joint strength obtained with the phenol resin on aluminum bonds after aging at 600° F was among the highest obtained in this investigation and was comparable to several other polymers which also had high resistance to thermal aging. These other polymers were polyamide PA-1, series 22; polyamide PA-2, series 23; adhesive FPL-878; a combination of phenol and epoxy resins, series 39; a combination of polyamide PA-1 and allyl glycidyl ether, series 49; and an adhesive composed of polyamide PA-1, diallyl melamine and paraform, series 51.

The resistance of this phenol resin to thermal deterioration in bonds of stainless steel, however, was extremely low. Deterioration of the adhesive was apparent from the reduction in joint strength and the

presence of discolorations in the bond areas after aging at temperatures as low as 450° F. Complete deterioration was noted when bonds were aged at 550° F. These results on bonds to stainless steel and aluminum pointed quite conclusively to an adverse catalytic effect of the steel on the thermal stability of the phenol-formaldehyde resin.

Melamine-formaldehyde-resin (ser. 17).- Probable chemical structure:
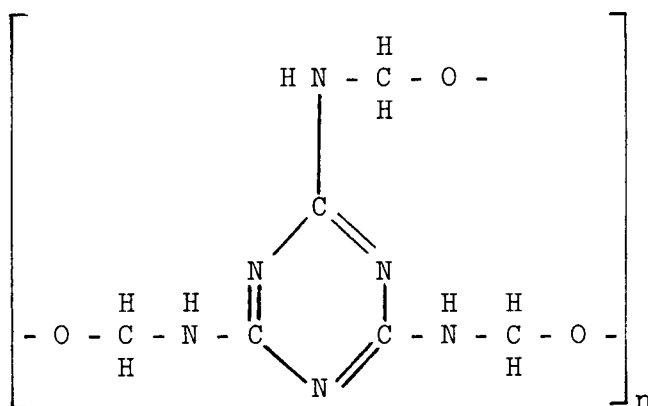
This melamine-formaldehyde resin (M-1) had moderate initial joint strength on aluminum and low strength on stainless steel. The adhesive was extremely brittle even after initial curing at 320° F and became more brittle with aging at elevated temperatures. Although the joint strength values were low for the aged adhesives, particularly on steel, thermal deterioration of the adhesive as indicated by pronounced discoloration in bonds did not occur until bonds were aged for 100 hours at 550° F.

Epoxy resins.- Probable chemical structure:
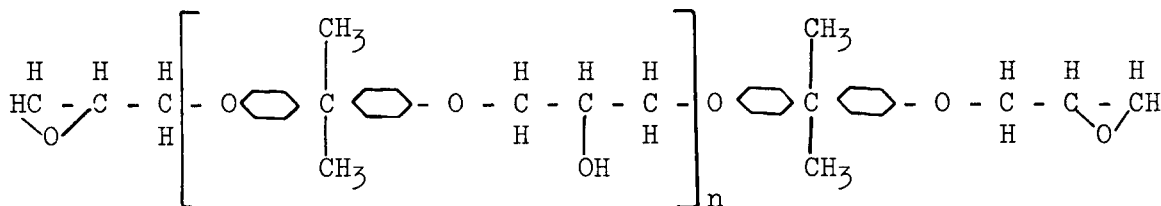
The epoxy resins E-1(ser. 18), E-2(ser. 19), and E-3(ser. 20) employed were reported to be condensation products of bisphenol A (2,2-diphenylol propane) with epichlorohydrin and varied in molecular weight and epoxide equivalent (ref. 3). In the above structural formula for epoxy resins the value of $\underline{n}$ is approximately 0 for E-1 resin, 2 for E-2 resin, and 9 for E-3 resin. The resins were used as adhesives without the addition of curing agents. Further condensation or polymerization of the

resins was obtained by curing the bonds initially for 16 hours at 450° F.
The results of this series of tests on aluminum and stainless steel bonds
made with these resins are presented graphically in figures 1 and 2.
The joint strength at room temperature before aging was always higher
in bonds on aluminum than in bonds on stainless steel. A higher level
of strength, however, was noted for resins E-1 and E-3 in bonds to stain-
less steel than in bonds to aluminum, after they were aged for 100 hours
at 450° F. After aging at 500° F, the epoxy resin bonds to stainless
steel were lower in strength in all cases than bonds to aluminum. The
aluminum bonds showed their greatest losses of strength when aged at
550° F and were almost completely deteriorated after 100 hours at 600° F
as were the bonds on stainless steel. In these tests of epoxy resins,
the lowest bond strength both initially and after heat aging was obtained
with resin E-1 which has the lowest molecular weight and lowest hydroxyl
equivalency but contains the highest epoxy equivalency of the epoxy resins
included in this work. The high epoxy content of the resin could con-
ceivably result in a high degree of crosslinkage between epoxy groups
during heating and result in an increase in embrittlement of the resin
and lower joint strength. The epoxy resins E-2 and E-3, on the other
hand, have appreciably lower epoxy equivalent contents than the E-1 resin
and higher hydroxy contents. Such compositions could produce both polymer
chain extensions through reactions of the terminal epoxy groups and cross-
linking reactions between the epoxy groups and the hydroxy groups. These
reactions could account for the higher joint strength obtained with the
E-2 and E-3 epoxy resins than was obtained with the E-1 resin.

The very similar behavior of the 3 resins in resistance to aging
at elevated temperatures, as evidenced by the marked losses in strength
after 100 hours at 500° F in bonds to stainless steel and after 100 hours
at 550° F in bonds to aluminum, suggests that some chemical bond inherent
in several epoxy resins investigated is thermally unstable at these tem-
peratures and results in deterioration of the polymer.

Epoxy resin from tetrahydroxy-phenylethane (ser. 21).- Probable
chemical formula:

This epoxy resin E-4 was reported to be made from 1,1-2,2- tetrakis
(4'-hydroxy phenyl)-ethane and epichlorohydrin. This resin differs

from the E-1, E-2, and E-3 resins in that the monomer unit could contain 4 reactive epoxy groups and be capable of a high degree of crosslinkage. The other primary difference in the resins was that E-4 was a tetra-substituted ethane derivative and the bisphenol resins were disubstituted propane derivatives. The results of bonding with E-4 showed the joint strength was low on both aluminum and stainless steel, indicating that the resin was probably extremely brittle. The results also showed that the E-4 resin was more resistant to aging at 550° and 600° F in bonds to aluminum than either of the bisphenol resins. This would indicate that the tetra-ethane group was more stable than the disubstituted propane group. The thermal resistance of stainless steel bonds, however, was not improved with E-4 resin and deterioration occurred at about the same temperature as the bonds made with bisphenol-A type of epoxy resins. The accelerated deterioration of the epoxy resin bonds by stainless steel presumably occurred then in some chemical structure that was common to both types of epoxy resins.

Polyamide resins.- Probable chemical structure:

$$H\left[\begin{array}{cccccc} & H & & H & \overset{O}{\overset{\|}{C}} & & \overset{O}{\overset{\|}{C}} \\ - & N & - R - & N & - C & - R - & C & - \end{array}\right]_n OH$$
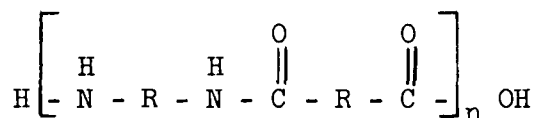
These polyamide resins PA-1(ser. 22), PA-2(ser. 23), and PA-3(ser. 24), all showed excellent resistance to thermal deterioration on both metals. The resin PA-3 had low strength after aging at 600° F. The actual chemical structure of these polymers was not known; however, they were all of the alcohol-soluble type. The results of the tests show conclusively, however, that the polyamide structures have high resistance to thermal degradation and indicate that N-substituted amide groups in an aliphatic chain contribute to increased thermal resistance but free amide groups as side groups to an aliphatic chain such as in polyacrylamide, series 2, produce a structure that is exceedingly low in thermal resistance. The results also suggest the need for further research of the polyamide resins to establish closer correlation between chemical structure and thermal behavior.

Mixture of phenol-formaldehyde resin and polyacrylamide (ser. 25).- This mixture of phenol-formaldehyde resin and polyacrylamide was formulated to provide approximately 2 hydroxyl groups from the phenol resin, P-1, for each amino group of the polyacrylamide (PAA-1). The mixture which was not compatible was considerably lower in joint strength after heating than the phenol resin alone in series 16. The thermal resistance properties of the mixture were more like those obtained with the polyacrylamide of series 2 that showed a high percentage of char after 100 hours at 450° F.

Mixture of phenol-formaldehyde and acrylonitrile-acrylamide copolymer (ser. 26).- This mixture of phenol-formaldehyde resin (P-1) and acrylonitrile-acrylamide copolymer (C-2) was formulated to provide 2 hydroxyl groups from the phenol resin, for each amino group in the copolymer. Thermal resistance in either aluminum or stainless steel bonds was generally lower than for either resin separately as in series 3 and 16, which would indicate that there was probably no crosslinkage occurring between the two resins, and the low thermal resistance of the copolymer of series 3 had an adverse effect on the performance of the phenol resin of series 16, even in the bonds of aluminum.

Mixture of phenol-formaldehyde resin and ethylacrylate-methacrylamide copolymer (ser. 27).- The two resins, phenol-formaldehyde (P-1) and ethylacrylate-methacrylamide copolymer (C-3), were combined in order to give approximately one potentially reactive hydroxyl group from the phenol resin, of series 16, for each amino group in the copolymer. Although this mixture contained only 10 percent of phenol resin, the strength of aluminum and stainless steel bonds both before aging and after 100 hours at 450° and 500° F was much higher than the strength of bonds obtained with the copolymer alone as in series 4. Bonds aged at 550° and 600° F lost nearly all their strength.

Mixture of phenol-formaldehyde resin and ethylacrylate-maleic anhydride copolymer (ser. 28).- The resins, phenol-formaldehyde (P-1) and ethylacrylate-maleic anhydride copolymer (C-4), were combined to provide approximately two hydroxyl groups of the phenol resin for each anhydride group of the copolymer. The strength of bonds without aging at the elevated temperature was improved over that obtained with the copolymer alone as in series 6. Resistance to thermal deterioration was low, however, even in bonds of aluminum. This indicated that there was probably no reaction between the anhydride of the copolymer and the hydroxyl groups of the phenol resin, which might be expected to form a more thermally stable chemical bond.

Mixture of phenol-formaldehyde resin and ethylacrylate-acrylonitrile copolymer (ser. 29).- Equal parts by weight of phenol-formaldehyde resin (P-1) and ethylacrylate-acrylonitrile copolymer (C-8) were arbitrarily used in this formulation because the ester and nitrile side groups were assumed to be unreactive with the phenol resin. The results of bond tests showed that this combination of resins was low in resistance to thermal deterioration even at 450° F and that the thermal resistance was quite similar to that observed with the copolymer alone as in series 10.

Mixture of phenol-formaldehyde resin and acrylonitrile-butadiene copolymer (ser. 30 and 31).- Adhesives, based on combinations of certain phenol resins with nitrile rubbers, have previously shown fairly good resistance to thermal deterioration in aluminum bonds at 450° F (ref. 4). In the present work, the phenol resin P-1 and the buna-N rubber copolymers

(C-10 and C-11) were used in equal amounts by weight so that approximately one hydroxyl group would be available from the phenol resin for each unsaturated double bond in the copolymer. Tests on the copolymers alone, series 13 and 14, showed that these materials had high resistance to thermal deterioration in bonds to aluminum and stainless steel after 100 hours at 550° F and the copolymer with the greater amount of butadiene had superior properties. When the phenol resin was combined with the elastomers, the thermal resistance was reduced as shown by lower joint strength and increased percentages of char. The decreases in resistance to thermal deterioration were particularly evident in bonds to stainless steel which very likely show the influence of the phenol resin on thermal resistance (see ser. 16). The formulation employing C-11 with the greater amount of butadiene was superior to the formulation with C-10 in bonds on stainless steel which again indicated that unsaturated carbon-to-carbon bonds in polymers are associated with increased resistance to thermal deterioration. The results of tests also showed no significant evidence of crosslinkage between the hydroxyl and unsaturated carbon-to-carbon bonds of the respective resins.

Mixture of phenol-formaldehyde resin and phenol-nitrile rubber adhesive.- Phenol-nitrile rubber adhesive A-1 (ser. 32), which is reported to be comprised of buna-N rubber and a small amount of a phenol resin, had high strength in bonds to stainless steel and aluminum. The bonds resisted thermal deterioration in both metals at temperatures up to 550° F at which temperature there were only moderate dropoffs in strength but marked increases in percentages of charred area in the broken bonds. The addition of varying amounts of phenol resin P-1 to the rubber adhesive (A-1) in series 33, 34, and 35 might be expected to result in a progressive loss of thermal resistance in stainless steel bonds as the phenol resin component increased. This trend, however, was negligible in the results of steel bonds tested after aging at 550° F for 100 hours. Combining these resins, instead, appeared to have more the effect of shielding or protection of the phenol resin against deterioration by the buna-N rubber, as shown by the similarity in joint strength of steel bonds after aging at 550° F in series 33, 34, and 35. The combination of the buna-N rubber with phenol resin therefore resulted in improved thermal resistance in stainless steel bonds over that obtained with phenol resin alone as used in series 16. Another commercially prepared adhesive, A-2, which is a specially formulated composition of buna-N rubber and phenol resin for metal bonding, had very good strength properties and high resistance to thermal deterioration at temperatures up to 600° F as in series 36. This commercial adhesive was formulated as a high-strength adhesive and thus had both considerably higher initial strength, and more strength after heat aging, compared to those formulations of the laboratory polymer series. These results were a further indication that buna-N rubber has a retarding effect on the deterioration of the phenol resin component.

Mixture of phenol-formaldehyde resin and epoxy resins.- The epoxy
resins (E-2 and E-4) and phenol-formaldehyde (P-1) resin were considered
to be potentially reactive with each other through the available hydroxy
and epoxy groups of the epoxy resin and the hydroxy and methylol groups
of the phenol resin. In series 37 and 38 the ratio by weight of the
resins was adjusted to provide approximately one hydroxyl group from the
phenol resin for each hydroxyl group of the epoxy resin, and two hydroxyl
groups from the phenol resin for each epoxy group of the epoxy resin.

In the combination of phenol resin P-1 with epoxy resin E-4 as in
series 37, the strength of bonds to aluminum after aging was generally
higher and the bonds contained a lower percentage of char than bonds of
the epoxy resin alone of series 21. Resistance to thermal deterioration
was high in bonds to aluminum even at 600° F but extremely low in bonds
to stainless steel at a temperature of 500° F.

In series 38 where E-2 was combined with the phenol resin P-1, the
strength of aluminum bonds after aging of the specimens for 100 hours at
500° F and 600° F was also markedly higher than the strength obtained
with epoxy resin alone of series 19 and quite comparable with results
for series 37. Bonds to stainless steel showed an abrupt loss in strength
when aged at 500° F but were still superior in strength after aging at
550° F to the combination of resins employing epoxy resin E-4 as in
series 37 and to the bond strength obtained with the phenol resin P-1
alone in series 16.

The results obtained with FPL 878 (ref. 5), as used in series 39,
were similar to the results shown in series 37 and 38. This FPL 878,
a heat-resistant adhesive specially formulated for bonding aluminum, is
basically a combination of phenol resin P-1 and epoxy resin E-3 that was
mixed at a ratio of 12 parts by weight of phenol resin to 2 parts by
weight of epoxy resin. The strength of FPL-878 bonds to aluminum after
aging 100 hours at 550° and 600° F was far superior to the strength
obtained with E-3 resin alone used in series 20, but bonds of stainless
steel were low in thermal resistance at 550° and 600° F.

The improved resistance to thermal deterioration at 500° to 600° F
in bonds to aluminum observed with combination of the epoxy and phenol
resins as compared to the resistance of epoxy resins alone indicated
that the chemical bond formed between resins in crosslinking was con-
siderably more thermally stable than bonds formed through intercross-
linked epoxy resins. This could mean that the bond formed between an
epoxy group and a hydroxy group was more stable than the bond formed in
the reaction of two epoxy groups. The low resistance of bonds of stain-
less steel to thermal deterioration again suggested a catalytic effect
by the steel.

<u>Mixture of phenol-formaldehyde resin and polyamide resin (ser. 40 and 41)</u>.- The phenol-formaldehyde resin (P-1) and polyamide resin (PA-1) were combined in series 40 to provide one hydroxy group from the phenol resins for each amino hydrogen in the polyamide resin. The results of bonding with PA-1 resin of series 22 had revealed that this polyamide resin had an exceptionally high resistance to thermal deterioration in bonds to aluminum and stainless steel. The combination with phenol resin, however, was lower in strength than the straight polyamide but still showed high thermal resistance in bonds to aluminum as reflected by the low percentages of charred area in the bonds. The bonds to stainless steel were low in thermal resistance and in this respect were similar to bonds made with phenol resin P-1 as in series 16. A formulation employing an excess of phenol resin, P-1, as in series 41 had similar properties (table 1). In combination with phenol resin, the polyamides differed markedly in their performance from that of the acrylonitrile-butadiene copolymer adhesives A-1 and A-2 in series 32 to 36 that appeared to have a shielding or protecting effect on deterioration of the phenol resin in bonds of stainless steel.

The polyamides conceivably polymerize further during heat aging with the formation of N-substituted amide groups by the reaction of carboxyl with primary or secondary amine groups without loss in heat resistance. The potential reaction of phenol resin with polyamide resins, however, to form tertiary-substituted nitrogen groups through the reaction of hydroxyl groups from the phenol resin with the primary and secondary amino groups of the polyamide presumably resulted in a crosslink of lower thermal stability than the amide link.

<u>Mixture of epoxy resin and polyacrylamide resin (ser. 42)</u>.- Epoxy (E-2) and polyacrylamide (PAA-1) resins were combined to investigate the effects of potential crosslinking reactions of the amide group and the epoxy groups of the resins at a ratio of approximately one epoxy group for each amino hydrogen. Joint strength of the combination was higher after aging of the specimens than when the polyacrylamide was used alone as an adhesive as in series 2 but was considerably lower than for the epoxy resin of series 19. The increased strength as compared to that of the polyacrylamide alone was very likely due to the high proportion of epoxy resin in the formulation. There was no evidence of extensive crosslinking between the two resins.

<u>Mixture of epoxy resin and ethylacrylate-methacrylamide copolymer (ser. 43)</u>.- The copolymer (C-3) of ethylacrylate and methacrylamide was combined with the epoxy resin (E-2) for the same reasons as in series 42, that of reacting epoxy groups with amide groups. This combination, however, employed a more desirable solvent system of methyl ethyl ketone and toluene which would be less reactive with the chemical groups in the resins than the water and alcohol system found to be necessary with the polyacrylamide-epoxy system of series 42. The results of tests showed

that both bonds to aluminum and stainless steel were low in resistance
to thermal deterioration. On the basis of results obtained in this
series and in series 44, it may also be concluded that the low thermal
instability of this adhesive composition was probably not due to the
breakdown of the ethylacrylate component but to the deterioration of
the methacrylamide component of the copolymer.

Mixture of epoxy resin and ethylacrylate-maleic anhydride copolymer
(ser. 44).- This combination of epoxy (E-2) and ethylacrylate-maleic
anhydride copolymer (C-4) resins was investigated to study the effect of
the possible crosslinkage of the epoxy resin and this copolymer such as
through the potential reaction of anhydride groups with epoxy groups,
to form ester linkages between polymers. The result was an exceptionally
stable, high-strength adhesive bond which resisted heating for 100 hours
at 550° F on both aluminum and stainless steel. Aging of the specimens
for 100 hours at 600° F, however, resulted in almost complete deteriora-
tion of the bonds, particularly on steel. The results of these tests
indicated that, when combined with the epoxy resin, the ethylacrylate
component of the copolymer was not deteriorated at temperatures up to
550° F. Bond strength was higher and percentages of char were lower in
bonds to stainless steel than to aluminum aged up to 550° F, indicating
a thermal stability effect of the ester linkages toward stainless steel
surfaces. When this copolymer was combined with phenol resin as in
series 28 or used alone as the bonding agent as in series 6, bonds showed
effects of thermal deterioration after exposure to 450° F. These results
would suggest that the maleic anhydride component itself had low thermal
resistance and that ester linkages to the phenol resin, if formed, were
also low in resistance to thermal deterioration.

Mixture of epoxy resin and ethylacrylate-acrylonitrile copolymer
(ser. 45).- The combination of epoxy resin (E-2) and the copolymer (C-7)
of ethylacrylate and acrylonitrile was used to evaluate the possible
crosslinking reaction between nitrile and epoxy groups. Results of tests
indicated that there possibly was a reaction between the resins since
the initial strength of bonds and strength after heat aging, on steel,
were higher than the strength of bonds obtained with polymers used
individually as adhesives as in series 9 and 19. The crosslinking
reaction may involve nitrile groups that rearrange at temperatures
above 200° C (ref. 6) to form imino groups which could then react with
the epoxy group. There was no evidence, however, of a reaction between
nitrile groups and hydroxyl groups when the copolymer was combined with
phenol resin in series 29.

Mixture of epoxy resin and acrylonitrile-butadiene copolymer
(ser. 46).- This combination of epoxy resin (E-2) and acrylonitrile-
butadiene copolymer (C-11) was investigated for effects of a possible
reaction between epoxy and hydroxy groups with nitrile and unsaturated
double bonds. The results were not promising. The thermal resistance

as indicated by the percentage of charred area was quite similar to the behavior observed in the epoxy resin used alone as the bonding agent as in series 19. Results after heat aging were considerably poorer, particularly on steel, than with the acrylonitrile-butadiene copolymer alone used for series 14.

Mixture of epoxy resin and polyamide resin (ser. 47 and 48).- The formulations employing polyamide PA-1 with either epoxy resin E-2 or E-4, were high in strength and resistance to thermal deterioration in bonds on both aluminum and stainless steel at temperatures up to 550° F. Bonds after aging at 600° F, however, were low in strength and showed a high degree of thermal deterioration. At a temperature of 550° F, bonds showed some increase in the percentage of bond area with char, particularly in bonds of aluminum which, with better joint strength, indicated that the thermal resistance of these resins was greater in bonds of stainless steel. The epoxy resins, E-2 in series 19 and E-4 in series 21, when used alone as adhesives had low strength after aging at 550° F, but the combinations of these epoxy and polyamide resins were much improved in strength and resistance to thermal deterioration at 550° F. These results would indicate that crosslinking of the two resins through reaction of the amino hydrogen of the amide group or end carboxyl groups with the epoxy groups formed a more thermally stable bond than when the epoxy groups react with themselves. The presence of carboxyl groups in the polyamide resin, which are also potentially reactive with the epoxy resin to form ester crosslinkages, could very likely account for the increase in thermal resistance as was observed when anhydride and epoxy groups were combined in series 44. Amide or carboxyl groups in the polyamide chain formed a more stable combination with epoxy resin than when the amide groups were present as side groups in polyacrylamide and reacted with epoxy resin in series 42. This would suggest that ester crosslinkages are more stable than amino crosslinkages. When polyamide resins were combined with phenol resins in series 40 and 41, the adhesive bonds to stainless steel were very low in resistance to thermal deterioration at 550° F, which reflects a very marked difference in the reaction of polyamide resin with the phenol resins and that obtained with the epoxy resin.

Mixture of polyamide resin and allyl glycidyl ether (ser. 49).- The polyamide resin (PA-1) was also mixed with the allyl glycidyl ether. It is possible that such allyl glycidyl ether groups could first react with either carboxyl or amino groups of the polyamide to form side chains still retaining active double bonds of carbon-to-carbon. These unsaturated side chain groups could then provide a means of crosslinking through additional polymerization with other allyl groups or could provide a chemical bond to the stainless steel surface as was postulated in studies on formulations of butadiene copolymers in series 13 and 14. The results of tests, however, showed no improvement in joint strength or thermal resistance over that obtained with the polyamide PA-1 resin alone in series 22.

Mixture of polyamide resin and allyl glycidyl ether and butadiene copolymer (ser. 50).- This formulation of polyamide (PA-1), allyl glycidyl ether, and butadiene copolymer showed the effect of adding butadiene-acrylonitrile copolymer (C-11), as used in series 14, to the adhesive composition studied in series 49 that contained equal parts of polyamide PA-1 and allyl glycidyl ether. It was thought that in this composition the allyl glycidyl ether could possibly serve as a crosslinking agent between the polyamide and unsaturated copolymer, such as with the epoxy group reacting with the amide or carboxyl groups, and the allyl group uniting with the unsaturated double bond of the butadiene. The results of tests were promising, particularly in bonds to stainless steel where high resistance to thermal deterioration was obtained at temperatures of 550° and 600° F. Thermal resistance was lower in bonds on aluminum which suggests that the copolymer was more stable in bonds on steel than aluminum, a condition that was also indicated from the results obtained with unsaturated copolymer alone as the bonding agent in series 14.

Mixture of polyamide resin, diallyl melamine, and paraformaldehyde (ser. 51).- In this adhesive composition of polyamide (PA-1), diallyl melamine, and paraformaldehyde, the paraformaldehyde was included in an attempt to produce methylol groups on the melamine that would be reactive with the amino hydrogens of the amide groups. In addition, the allyl groups could crosslink with each other or be free to form a strong bond to the steel surface. The results were particularly promising, as the composition was one of the few resin systems studied that had high initial strength and also good thermal resistance in bonds to aluminum and stainless steel at 600° F. The results also revealed a marked difference in the thermal resistance obtained when polyamide resins were reacted with a melamine-formaldehyde resin as compared with a phenol-formaldehyde resin as in series 40 and 41.

Mixture of polyamide resin and melamine resin (ser. 52).- Further research on the polyamide-melamine formulations with a composition of polyamide PA-1 and a conventional melamine-formaldehyde resin, M-1, did not yield as promising results as the formulation in series 51 with diallyl melamine. Results of tests were variable, which might have been due to the incompatability of the two resins. High joint strength, however, was obtained after aging the specimens at 550° F, which indicates that further study of the polyamide-melamine systems would be worthwhile.

Mixture of melamine resin and polyvinyl alcohol (ser. 53).- This mixture of melamine (M-1) and polyvinyl alcohol (PVA-1) resins had low strength and showed no resistance to thermal deterioration in bonds to stainless steel. The bond strength on aluminum joints was higher than was obtained with either resin used alone but was quite inferior to other more promising resin systems. The resins were combined to investigate the thermal characteristics of crosslinks between methylol groups of the melamine and hydroxyl groups of the polyvinyl alcohol.

Mixture of melamine resin and polyacrylamide (ser. 54).- This bonding formulation of melamine resin (M-1) and polyacrylamide (PAA-1) was made to investigate the thermal properties of crosslinks formed through methylol and amine groups. Results of tests showed a low order of strength to both metals and a low resistance to thermal deterioration.

Mixture of ethylacrylate-maleic anhydride copolymer and acrylonitrile-acrylamide copolymer (ser. 55).- The formulation of ethylacrylate-maleic anhydride (C-4) and acrylonitrile-acrylamide (C-2) copolymer resins was investigated because of the potential crosslinkage through the anhydride and amine groups. Because of the high thermal properties of the polyamide PA-1 it was expected that this resin blend of copolymers could conceivably have high thermal resistance due to the formation of amide crosslinks. A comparison of the results obtained with each copolymer used alone as an adhesive, as in series 3 and 6, showed that an increase in strength and thermal resistance after aging the bonded specimens at 450° F was obtained by employing the two copolymers in a blend, but on the specimens aging at 500° F and higher there were no such advantages of the mixture.

Mixture of ethylacrylate-acrolein copolymer and ethylacrylate-methacrylamide copolymer (ser. 56).- The formulation of ethylacrylate-acrolein (C-5) and ethylacrylate-methacrylamide (C-3) copolymers was investigated to study the possible effect of crosslinkage of the aldehyde and amino groups on strength and thermal resistance. These groups could conceivably form a substituted amide crosslink that, based on the knowledge of the performance of the polyamide PA-1 (series 22), would result in improved thermal properties. The result was an adhesive bond that had improved strength and thermal resistance in bonds to aluminum over that obtained with individual copolymers as in series 4 and 7 but still of a low order, particularly on stainless steel.

CONCLUSIONS

This investigation has provided further evidence of specific effects of metal surfaces accelerating the deterioration of adhesive bonds on aging for 100 hours at elevated temperatures, and also has provided an interesting correlation of polymer structure with temperature and with the nature of metal surfaces employed in the bond. Several different resins of varying chemical composition were found that possessed high resistance to thermal deterioration in bonds on both aluminum and stainless steel. These resins suggest promising approaches to the problem of developing an adhesive with improved heat-resistant properties in bonds to stainless steel. The major findings of research on heat aging may be summarized as follows:

(1) The phenol-formaldehyde resin had high thermal resistance in bonds on aluminum at 600° F but had deteriorated significantly in bonds on stainless steel at 450° F.

(2) Polyamide resins deteriorated significantly in bonds on stainless steel at 600° F but to a much less degree in bonds on aluminum.

(3) Epoxy resins (bisphenol type) deteriorated at 550° F in bonds on aluminum and stainless steel with evidence of much more deterioration in steel than in aluminum bonds at 500° F.

(4) Epoxy resin (tetraphenyl-ethane type) deteriorated at 550° F in bonds to stainless steel but had relatively high resistance at 600° F in aluminum bonds and was definitely superior to the bisphenol-type resins.

(5) Polybutadiene-acrylonitrile copolymers appeared to have higher resistance to thermal deterioration in bonds to stainless steel than in bonds to aluminum at 550° to 600° F. Thermal resistance of these copolymers improved as the amount of butadiene in the copolymer increased.

(6) A series of other vinyl copolymers with varying side groups consisting of ethyl chloride, ethyl esters, nitrile, amide, anhydride, and aldehyde groups were low in bond strength and appeared to be quite similar in thermal resistance in both bonds to aluminum and stainless steel.

(7) In bonds of stainless steel where the single polymer systems were used as adhesives, the butadiene-acrylonitrile copolymer and the polyamide resins had the greatest resistance to thermal deterioration at 550° and 600° F. All other polymer materials examined had little or no strength in stainless steel after aging at these temperatures. These results revealed that polymers with unsaturated carbon-to-carbon and amide groups in the polymer chain had the greatest thermal stability in bonds to stainless steel.

(8) In bonds to stainless steel the phenol-formaldehyde resins and epoxy resins were almost completely deteriorated at 550° and 600° F, indicating that the stainless steel surfaces accelerated deterioration of these resins.

(9) Combinations of phenol-formaldehyde resin with butadiene copolymers, particularly those mixtures with a relatively high proportion of the butadiene copolymer, had high resistance to aging for 100 hours at 550° F in bonds to stainless steel and to aluminum. A commercial adhesive of this type, A-2, was quite resistant to aging at 600° F.

(10) Combinations of phenol-formaldehyde resin with bisphenol-type epoxy resins were high in resistance to thermal deterioration at 600° F

in bonds to aluminum but were only resistant to 500° F in bonds to stainless steel. The improvement in thermal resistance of this combination of resins over the epoxy resin alone at 600° F in bonds on aluminum indicated a possible crosslinking of the 2 resins that resulted in improved thermal stability. The low thermal resistance in bonds to stainless steel of the combined phenol and epoxy resins again indicated a specific adverse effect of the stainless steel on these aromatic-type resins.

(11) Combinations of phenol-formaldehyde resin with polyamide resin showed rather marked deterioration in bonds to stainless steel at 500° F and above, but these combinations were quite stable in bonds to aluminum. A decrease in the thermal resistance in bonds to stainless steel made with the combined resins, below that observed in bonds with the straight polyamide resin, indicated that the phenol resin may have contributed to the deterioration of the combination and that the polyamide was probably not forming a thermally stable bond to the reactive components of the steel surface.

(12) A comparison of the results of combining phenol resin with butadiene copolymer, epoxy resin, or polyamide resin suggested that the high thermal resistance of the phenol-butadiene adhesives could possibly be due to the butadiene reacting with the metal surface to form a thermally stable metallo-organic type of compound. This thermally stable compound thus could have deactivated the metal component causing deterioration and thus account for the improved thermal resistance of the phenol resin component.

(13) A formulation composed of epoxy resin and ethylacrylate-maleic anhydride copolymer, although each resin by itself had extremely low resistance to aging at 550° F, had exceedingly high thermal resistance at this temperature, particularly in bonds to stainless steel. These results suggest that the ester crosslink, presumably formed between the epoxy and anhydride group of the resins, was a highly stable group and resisted the specific accelerated deterioration effects of the stainless steel surface, and thus improved the overall thermal resistance of both polymer chains. This combination of resins, however, was almost completely deteriorated at 600° F.

(14) Combinations of epoxy resin with polyamide resins were similar to the epoxyanhydride copolymer combination. High thermal resistance was obtained in bonds to stainless steel at 550° F with considerably lower levels of performance in aluminum bonds. Aging at 600° F caused almost complete deterioration of the bonds. These results indicated that the epoxy resin was possibly forming stable ester crosslinks with the carboxyl end groups of the polyamide resin.

(15) When epoxy resins were combined with a vinyl copolymer containing amide side groups, the resistance to thermal deterioration was low, indicating that probably such amine crosslinkages, if formed, were not heat stable.

(16) A combination of polyamide resin, butadiene-acrylonitrile copolymer, and allyl glycidyl ether was quite outstanding in thermal resistance at 600° F in bonds to stainless steel and to a lesser degree to aluminum. These results indicated again the high thermal resistance possible when unsaturated double bonds, amide chains, and ester crosslinkages were likely to be present.

(17) A combination of polyamide resin with diallyl melamine and paraformaldehyde was another outstanding formulation with high resistance to thermal deterioration at 600° F in bonds to stainless steel and to aluminum. The composition of this formula suggested that crosslinkages occurred between the polyamide and melamine with further possibility of crosslinkages through the allyl groups.

Forest Products Laboratory,
    Madison, Wis., July 2, 1958.

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W-114

TABLE 1.-- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES

Series no.	Chemical composition of polymer[1]	Curing condition[2]	Aging temperature,[3] °F	Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
1	Methylacrylate (95 percent) and chloro-ethylvinylether (5 percent) (C-1); 9.4 percent solution in 9 parts of MEK and 1 part of TOL	A	80	532	0	0	366	0	0
			450	1,332	16	14	490	0	19
			500	1,288	0	56	746	44	42
			550	48	0	100	6	0	100
			600	106	6	82	0	0	100
2	Polyacrylamide (PAA-1); 20 percent solution in water	B	80	388	0	0	902	0	0
			450	6	0	88	72	1	94
			500	22	2	78	0	0	100
			550	18	3	99	58	0	100
			600	36	2	100	0	0	100
3	Acrylonitrile (75 percent) and acrylamide (25 percent) (C-2); 20 percent solution in DMF	B	80	112	10	0	210	10	0
			450	0	10	100	0	0	100
			500	0	0	100	10	0	100
			550	0	0	100	2	0	100
			600	0	14	100	0	0	100
4	Ethylacrylate (95 percent) and methacrylamide (5 percent) (C-3); 7.1 percent solution in 9 parts of MEK and 1 part of TOL	A	80	160	12	0	158	12	0
			450	162	0	54	162	0	16
			500	220	0	28	140	0	59
			550	60	0	100	16	0	100
			600	186	12	66	0	0	100
5	Polyethylacrylate (PEA-1); 20 percent solution in 9 parts of MEK and 1 part of TOL	B	80	128	0	0	104	0	0
			450	172	0	5	214	0	5
			500	252	0	22	40	0	14
			550	62	0	46	16	0	100
			600	280	55	68	0	0	100
6	Ethylacrylate (95 percent) and maleic anhydride (5 percent) (C-4); 6 percent solution in nitroethane	A	80	216	17	0	182	10	0
			450	256	0	84	106	0	86
			500	116	0	66	82	0	71
			550	42	0	100	14	0	100
			600	28	20	90	0	0	100
7	Ethylacrylate (97.5 percent) and acrolein (2.5 percent) (C-5); 9.5 percent solution in 9 parts MEK and 1 part TOL	A	80	60	0	0	56	0	0
			450	204	0	52	268	0	22
			500	208	0	45	270	48	55
			550	36	0	82	20	0	100
			600	0	0	100	0	0	100
8	Ethylacrylate (95 percent) and acrylonitrile (5 percent) (C-6); 7.8 percent solution in 9 parts of MEK and 1 part of TOL	A	80	218	84	0	224	96	0
			450	228	86	10	300	90	4
			500	396	30	43	234	0	42
			550	40	10	100	16	10	100
			600	212	52	83	0	0	100

[1] The letter and number appearing in parenthesis after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2] The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens:
A is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
A-1 is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
B is 30 minutes at 400° F and 200 pounds per square inch bonding pressure.
B-1 is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
C is 16 hours at 400° F at contact pressure (heated in oven).
D is 60 minutes at 350° F and 250 pounds per square inch bonding pressure.
E is 16 hours at 450° F at contact pressure (heated in oven).

[3] Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.

[4] Shear strength in pounds per square inch. Average of tests on 5 or more specimens.

[5] Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.

[6] Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.

W-114

TABLE 1.- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES - Continued

Series no.	Chemical composition of polymer[1]	Curing condition[2]	Aging temperature[3], °F	Average test values for joints of -					
				Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
9	Ethylacrylate (75 percent) and acrylonitrile (25 percent) (C-7); 7.2 percent solution in 9 parts MEK and 1 part TOL	A	80	1,312	100	0	1,142	96	0
			450	1,824	18	18	980	18	28
			500	260	20	68	106	0	86
			550	12	0	100	0	0	100
			600	16	0	100	0	0	100
10	Ethylacrylate (50 percent) and acrylonitrile (50 percent) (C-8); 16.7 percent solution in DMF, MEK, TOL	B	80	2,128	32	0	5,376	18	0
			450	122	100	82	94	8	98
			500	36	0	100	32	0	99
			550	14	0	100	28	0	100
			600	0	0	100	0	0	100
11	Ethylacrylate (15 percent) and acrylonitrile (85 percent) (C-9); 25 percent solution in DMF	B	80	184	82	0	1,020	86	0
			450	0	0	100	0	0	100
			500	24	0	100	10	0	100
			550	24	0	100	42	0	100
			600	22	0	100	0	0	100
12	Polyacrylonitrile (PAN-1); 10 percent solution in DMF	B	80	0	100	0	0	100	0
			450	No adhesion to metal	No adhesion to metal	No adhesion to metal	No adhesion to metal	No adhesion to metal	No adhesion to metal
			500						
			250						
			600						
13	Acrylonitrile (35 percent) and butadiene (65 percent) (C-10); 5 percent solution in DMF, MEK, and TOL	B	80	182	28	0	127	60	0
			450	----	----	----	----	----	----
			500	1,066	44	21	903	45	25
			550	892	6	49	1,260	5	58
			600	112	12	96	244	0	97
14	Acrylonitrile (25 percent) and butadiene (75 percent) (C-11); 5 percent solution in DMF, MEK, TOL	B	80	269	47	0	215	45	0
			450	1,780	25	7	1,873	26	7
			500	1,057	50	12	1,105	57	10
			550	1,058	9	5	1,414	10	58
			600	373	34	45	711	6	96
15	Polyvinylalcohol (PVA-1); 15 percent solution in water	A	80	20	79	0	38	60	0
			450	0	0	100	0	0	100
			500	0	11	96	132	0	96
			550	0	0	100	10	8	95
			600	0	0	100	56	0	96
16	Phenol-formaldehyde resin (P-1); 40 percent solution in MA and EA	A	80	1,362	10	0	1,732	2	0
			450	1,290	12	19	588	29	52
			500	1,336	11	7	274	32	30
			550	980	13	11	0	6	100
			600	1,146	8	8	0	0	100
17	Melamine-formaldehyde resin (M-1); 67 percent solution in water	A	80	888	0	0	316	0	0
			450	212	0	0	0	0	0
			500	400	0	0	0	0	0
			550	16	0	40	0	0	100
			600	0	2	95	0	0	100
18	Epoxy resin (E-1); Heated resin applied to heated metal	C	80	2,264	0	0	1,720	24	0
			450	1,262	58	5	1,724	76	4
			500	658	38	26	628	12	47
			250	26	0	97	100	0	91
			600	14	0	99	0	0	100

[1] The letter and number appearing in parentheses after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2] The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens:
A   Is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
A-1 Is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
B   Is 60 minutes at 400° F and 200 pounds per square inch bonding pressure.
B-1 Is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
C   Is 16 hours at 400° F at contact pressure (heated in oven).
D   Is 60 minutes at 350° F and 250 pounds per square inch bonding pressure.
E   Is 16 hours at 450° F at contact pressure (heated in oven).

[3] Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.

[4] Shear strength in pounds per square inch. Average of tests on 5 or more specimens.

[5] Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.

[6] Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.

TABLE 1.- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES - Continued

Series no.	Chemical composition of polymer[1]	Curing condition[2]	Aging temperature,[3] °F	Average test values for joints of -					
				Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
19	Epoxy resin (B-2) Heated resin applied to heated metal	C	80	3,728	0	0	2,456	0	0
			450	3,464	0	1	2,320	0	10
			500	2,920	0	0	878	0	14
			550	120	0	91	220	0	100
			600	102	0	92	68	0	96
20	Epoxy resin (E-3) Heated resin applied to heated metal	C	80	3,472	0	0	2,392	0	0
			450	2,280	48	0	3,048	0	2
			500	1,520	8	2	618	0	16
			550	94	0	62	88	0	66
			600	182	0	92	32	0	98
21	Epoxy resin (B-4) Heated resin spread on heated metal	C	80	1,635	88	0	830	89	1
			450	610	95	25	796	12	89
			500	578	82	64	578	5	74
			550	706	88	95	218	4	97
			600	524	6	90	0	0	100
22	Polyamide resin (PA-1) 20 percent solution in MA	B	80	1,480	0	100	2,016	14	0
			450	1,230	10	9	2,440	7	13
			500	2,050	8	23	1,936	12	14
			550	1,782	7	9	1,486	6	40
			600	1,288	2	44	446	4	85
23	Polyamide resin (PA-2) 20 percent solution in MA	B	80	2,608	8	0	2,184	16	0
			450	1,592	6	9	1,588	9	2
			500	----	--	--	----	--	--
			550	2,460	0	1	1,588	10	33
			600	1,352	1	30	328	6	80
24	Polyamide resin (PA-3) 20 percent solution in MA	B	80	2,512	7	0	1,736	18	0
			450	1,098	0	18	2,064	4	43
			500	----	--	--	----	--	--
			550	1,368	1	24	1,390	6	58
			600	96	2	95	56	0	99
25	Polyacrylamide (PAA-1) 1.0 part Phenol resin (P-1) 2.4 parts (See series nos. 2 and 16) 21 percent solution in water, MA, and EA (incompatible)	A	80	1,566	8	0	2,044	5	0
			450	628	3	62	164	0	90
			500	286	20	85	152	41	90
			550	118	2	100	2	0	100
			600	2	0	100	0	0	100
26	Acrylonitrile (75 percent) and acrylamide (25 percent) (C-2) 1.4 parts Phenol resin (P-1) 1.0 part (See series nos. 3 and 16) 33 percent solution in MA and DMF	A	80	1,356	4	0	2,056	6	0
			450	216	1	62	150	5	71
			500	186	0	85	68	0	95
			550	72	0	100	62	0	100
			600	22	0	100	0	0	100

[1]The letter and number appearing in parenthesis after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2]The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens:
  A   is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
  A-1 is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
  B   is 30 minutes at 400° F and 200 pounds per square inch bonding pressure.
  B-1 is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
  C   is 16 hours at 400° F at contact pressure (heated in oven).
  D   is 16 minutes at 350° F and 250 pounds per square inch bonding pressure.
  E   is 16 hours at 450° F at contact pressure (heated in oven).

[3]Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.

[4]Shear strength in pounds per square inch. Average of tests on 5 or more specimens.

[5]Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.

[6]Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.

TABLE 1.- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES - Continued

Series no.	Chemical composition of polymer[1]	Curing condition[2]	Aging temperature,[3] °F	Average test values for joints of -					
				Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
27	Ethylacrylate (95 percent) and methacrylamide (5 percent) (C-5) 10.0 parts / Phenol resin (P-1) 1.0 part / (See series nos. 4 and 16) / 12.5 percent solution in MEK, TOL, and DMF	A	80	532	0	0	314	74	0
			450	708	1	4	462	20	12
			500	250	0	9	388	6	12
			550	6	0	36	46	0	74
			600	6	0	100	0	0	100
28	Ethylacrylate (95 percent) and maleic anhydride (5 percent) (C-4) 8.7 parts / Phenol resin (P-1) 1.0 part / (See series nos. 6 and 16) / 7.0 percent solution in MEK	A	80	1,064	0	0	581	31	0
			450	110	0	87	64	4	85
			500	80	12	64	0	2	87
			550	4	1	80	6	8	87
			600	140	1	88	0	0	100
29	Ethylacrylate (50 percent) and acrylonitrile (50 percent) (C-8) 1.0 part / Phenol resin (P-1) 1.0 part / (See series nos. 10 and 16) / 26 percent solution in MEK, TOL, and DMF	A	80	1,012	4	0	1,288	96	0
			450	200	5	22	328	0	48
			500	---	-	---	---	-	---
			550	20	3	100	28	2	100
			600	0	0	100	0	0	100
30	Acrylonitrile (35 percent) and butadiene (65 percent) (C-10) 1.0 part / Phenol resin (P-1) 1.0 part / (See series nos. 13 and 16) / 20 percent solution in MEK, TOL, and DMF (copolymer partially insoluble)	A	80	412	1	0	234	6	0
			450	1,084	14	27	452	16	52
			500	876	22	53	110	9	90
			550	804	10	45	180	0	99
			600	456	0	95	94	0	100
31	Acrylonitrile (25 percent) and butadiene (75 percent) (C-11) 1.0 part / Phenol resin (P-1) 1.0 part / (See series nos. 14 and 16) / 5 percent solution in MEK, TOL, and DMF (copolymer partially insoluble)	A	80	300	4	0	196	4	0
			450	988	50	5	660	9	26
			500	768	12	23	390	4	68
			550	742	30	38	62	0	93
			600	664	0	62	110	0	100
32	Phenol-nitrile rubber adhesive (A-1) (Commercial adhesive composed of buna-N rubber and a small amount of phenol resin)	A-1	80	1,360	22	0	1,690	0	0
			450	2,020	0	4	3,920	6	2
			500	1,552	10	21	1,852	7	22
			550	726	0	86	1,218	0	90
			600	132	0	96	324	14	93
33	Phenol-nitrile rubber adhesive (A-1) 2.0 parts / Phenol resin (P-1) 1.0 part / (See series nos. 16 and 32)	A-1	80	651	4	0	523	0	0
			450	1,149	18	18	1,579	38	3
			500	606	40	28	998	12	14
			550	474	1	45	406	2	69
			600	302	5	97	314	10	100
34	Phenol-nitrile rubber adhesive (A-1) 2.0 parts / Phenol resin (P-1) 2.0 parts / (See series nos. 16 and 32)	A-1	80	570	0	0	566	2	0
			450	779	0	8	1,351	37	0
			500	512	0	14	920	30	28
			550	418	0	37	452	2	34
			600	265	0	88	305	2	100

[1]The letter and number appearing in parenthesis after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2]The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens:
A   is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
A-1 is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
B   is 30 minutes at 400° F and 200 pounds per square inch bonding pressure.
B-1 is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
C   is 16 hours at 400° F at contact pressure (heated in oven).
D   is 60 minutes at 350° F and 250 pounds per square inch bonding pressure.
E   is 16 hours at 450° F at contact pressure (heated in oven).

[3]Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.

[4]Shear strength in pounds per square inch. Average of tests on 5 or more specimens.

[5]Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.

[6]Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.

W-774

TABLE 1.- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES - Continued

Series no.	Chemical composition of polymer[1]	Curing condition[2]	Aging temperature,[3] °F	Average test values for joints of -					
				Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
35	Phenol-nitrile rubber adhesive (A-1) 2.0 parts / Phenol resin (P-1) 3.0 parts (See series nos. 16 and 32)	A-2	80	384	4	0	602	0	6
			450	984	2	19	1,956	9	2
			500	862	0	29	1,070	12	33
			550	858	0	21	458	25	70
			600	458	1	60	116	6	100
36	Phenol-nitrile rubber adhesive (A-2) (Commercial metal bonding adhesive composed of phenol resin and buna-N rubber)	D	80	2,848	14	0	2,400	0	0
			450	2,028	10	1	1,074	18	60
			500	1,494	10	14	948	0	72
			550	1,044	0	94	878	0	80
			600	672	48	76	654	10	90
37	Epoxy resin (E-4) 1.0 part / Phenol resin (P-1) 1.0 part (See series nos. 16 and 21) 32 percent solution in MEK	A	80	1,180	4	0	1,948	1	0
			450	----	-	-	----	-	-
			500	964	0	14	126	0	85
			550	990	8	3	0	0	100
			600	756	6	25	0	0	100
38	Epoxy resin (E-2) 1.7 parts / Phenol resin (P-1) 1.0 part (See series nos. 16 and 19) 50 percent solution in MEK	A	80	304	15	0	662	3	0
			450	1,508	0	6	1,542	6	6
			500	924	4	6	592	7	29
			550	907	4	12	380	2	80
			600	696	4	40	42	0	100
39	FPL-878 adhesive / A laboratory adhesive composed of a phenol resin and an epoxy resin (See series nos. 16 and 20)	A	80	2,118	0	0	2,244	0	0
			450	1,510	0	8	1,662	0	10
			500	1,588	0	6	1,064	0	12
			550	1,404	0	10	72	9	91
			600	1,218	0	20	4	0	100
40	Polyamide (PA-1) 1.3 parts / Phenol resin (P-1) 1.0 part (See series nos. 22 and 16) 30 percent solution in MA	A	80	2,224	15	0	1,612	32	0
			450	----	-	-	----	-	-
			500	824	15	23	378	13	65
			550	548	32	25	168	8	72
			600	572	55	27	40	0	100
41	Polyamide (PA-1) 1.0 part / Phenol resin (P-1) 1.0 parts (See series nos. 22 and 16) 50 percent solution in MA	A	80	1,820	7	0	1,752	28	0
			450	----	-	-	----	-	-
			500	1,256	6	17	28	3	96
			550	1,002	31	24	0	0	100
			600	670	10	29	0	0	100
42	Polyacrylamide (PAA-1) 1.0 part / Epoxy resin (E-2) 12.5 parts (See series nos. 2 and 19) 50 percent solids dispersed in water and MA (incompatible mixture - spread while warm)	A	80	896	2	2	258	0	0
			450	772	0	59	324	0	85
			500	380	0	71	388	0	94
			550	116	0	97	152	0	100
			600	48	0	95	0	0	100

[1]The letter and number appearing in parenthesis after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2]The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens:
    A   is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
    A-1 is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
    B   is 30 minutes at 400° F and 200 pounds per square inch bonding pressure.
    B-1 is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
    C   is 16 hours at 400° F at contact pressure (heated in oven).
    D   is 60 minutes at 350° F and 250 pounds per square inch bonding pressure.
    E   is 16 hours at 450° F at contact pressure (heated in oven).

[3]Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.
[4]Shear strength in pounds per square inch. Average of tests on 5 or more specimens.
[5]Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.
[6]Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.

W-114

TABLE 1.- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES - Continued

Series no.	Chemical composition of polymer[1]	Curing conditions[2]	Aging temperature,[3] °F	Average test values for joints of -					
				Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
43	Ethylacrylate (95 percent) and methacrylamide (5 percent) (C-3) 1.9 parts; Epoxy resin (E-2) 1.0 parts; (See series nos. 4 and 19) 5 percent solution in MEK and TOL	A	80	468	1	0	700	0	0
			450	328	0	24	296	1	83
			500	80	0	98	38	0	100
			550	140	0	85	78	11	88
			600	182	4	82	82	0	100
44	Ethylacrylate (95 percent) and maleic anhydride (5 percent) (C-4) 5.0 parts; Epoxy resin (E-2) 1.0 part; (See series nos. 6 and 19) 15 percent solution in MEK	E	80	1,732	0	0	2,336	18	0
			450	1,612	5	50	2,304	7	7
			500	1,554	8	25	2,472	23	5
			550	1,296	26	27	2,400	56	2
			600	220	0	89	62	0	100
45	Ethylacrylate (75 percent) and acrylonitrile (25 percent) (C-7) 1.0 part; Epoxy resin (P-1) 1.4 parts; (See series nos. 9 and 19) 6 percent solution in MEK and TOL	E	80	956	0	0	3,424	0	0
			450	1,056	0	0	2,320	7	4
			500	810	0	0	1,348	15	30
			550	210	0	50	590	0	100
			600	62	0	30	0	0	100
46	Acrylonitrile (25 percent) and butadiene (75 percent) (C-11) 1.0 part; Epoxy resin (E-3) 7.0 parts; (See series nos. 14 and 19) 29 percent solution in MEK and TOL	B-1	80	244	0	0	494	0	0
			450	1,120	20	15	1,776	7	12
			500	716	31	16	1,148	25	23
			550	168	16	80	416	8	93
			600	64	4	100	6	0	100
47	Polyamide (PA-1) 1.0 part; Epoxy resin (E-2) 4.0 parts; (See series nos. 22 and 19) 29 percent solution in MA and B	A	80	1,516	14	0	1,760	7	0
			450	2,008	0	30	2,280	5	4
			500	1,832	0	21	1,782	3	27
			550	752	1	85	1,508	3	34
			600	508	0	86	8	0	100
48	Polyamide (PA-1) 1.37 parts; Epoxy resin (E-4) 1.0 part; (See series nos. 22 and 21) 29 percent solution in TOL, MA, and B	A	80	1,040	6	0	1,516	13	0
			450	790	3	25	3,168	6	1
			500	812	6	5	2,440	3	0
			550	636	4	90	1,164	4	30
			600	292	1	85	0	0	100
49	Polyamide (PA-1) 1.0 part; Allyl glycidyl ether 1.0 part; (See series no. 22) 50 percent solution in MA	A-1	80	600	1	0	616	6	0
			450	1,816	1	33	1,392	0	28
			500	1,744	0	42	1,580	4	41
			550	1,534	1	48	368	8	90
			600	1,236	3	86	192	0	99
50	Polyamide (PA-1) 1.0 part; Allyl glycidyl ether 1.0 part; Acrylonitrile (25 percent) and butadiene (75 percent) (C-11) 0.6 part; (See series nos. 49 and 22) 17 percent solution in MA, MEK, TOL, and DMF	A	80	1,444	0	0	2,524	8	0
			450	1,584	0	67	2,168	1	13
			500	1,502	2	76	1,254	16	41
			550	660	4	65	806	6	53
			600	212	10	95	656	8	65

[1] The letter and number appearing in parenthesis after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2] The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens.
A   is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
A-1 is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
B   is 30 minutes at 400° F and 200 pounds per square inch bonding pressure.
B-1 is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
C   is 16 hours at 400° F at contact pressure (heated in oven).
D   is 60 minutes at 350° F and 250 pounds per square inch bonding pressure.
E   is 16 hours at 450° F at contact pressure (heated in oven).

[3] Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.

[4] Shear strength in pounds per square inch. Average of tests on 5 or more specimens.

[5] Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.

[6] Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.

W-114

TABLE 1.- RESULTS OF LAP-JOINT TESTS ON METAL AT 80° F AFTER EXPOSURE TO VARIOUS AGING TEMPERATURES - Concluded

Series no.	Chemical composition of polymer[1]	Curing conditions[2]	Aging temperature,[3] °F	Average test values for joints of -					
				Aluminum			Stainless steel		
				Psi[4]	Percent[5]	Percent[6]	Psi[4]	Percent[5]	Percent[6]
51	Polyamide (PA-1) 3.3 parts Diallyl melamine 3.3 parts Paraformaldehyde 1.0 part (See series no. 22) 33 percent solution in MA	A	80 450 500 550 600	1,968 1,056 762 1,682 1,258	7 4 10 0 21	0 8 52 34 69	2,808 2,368 2,004 1,968 746	39 8 0 1 30	0 3 28 86 50
52	Polyamide (PA-1) 1.37 parts Melmac 401 1.0 part (See series nos. 22 and 17) 28 percent solution in water and MA (not compatible)	A-1	80 450 500 550 600	2,304 576 376 968 456	25 8 4 10 26	0 29 64 88 90	2,160 536 376 1,340 182	0 0 0 0 0	0 74 96 65 49
53	Polyvinyl alcohol (PVA-1) 1.0 part Melamine-formaldehyde resin (M-1) 2.0 parts (See series nos. 15 and 17) 37 percent solution in water	A	80 450 500 550 600	948 564 544 140 108	15 3 14 0 0	0 43 65 100 91	156 0 0 0 0	95 0 98 70 56	0 100 100 100 100
54	Polyacrylamide (PA-1) 1.0 part Melamine-formaldehyde resin (M-1) 1.2 parts (See series nos. 2 and 17) 26 percent solution in water and MA	A	80 450 500 550 600	488 2 150 16 80	8 6 0 0 0	0 0 93 100 98	64 2 0 0 0	28 24 31 0 0	0 24 93 100 100
55	Ethylacrylate (95 percent) and maleic anhydride (5 percent) (C-4) 3.0 parts Acrylonitrile (75 percent) and acrylamide (25 percent) (C-2) 1.0 part (See series nos. 6 and 3) 4 percent solution in DMF	B	80 450 500 550 600	148 350 100 0 4	0 0 1 0 0	0 61 64 100 100	196 628 96 32 0	0 0 0 0 0	0 54 52 100 100
56	Ethylacrylate (95 percent) and acrolein (5 percent) (C-5) 1.5 parts Ethylacrylate (95 percent) and meth-acrylamide (5 percent) (C-3) 1.0 part (See series nos. 7 and 4) 5 percent solution in MEK and TOL	B	80 450 500 550 600	94 360 764 24 344	0 0 2 4 0	0 6 40 96 64	72 278 204 0 0	0 0 2 0 0	0 13 44 94 100

[1]The letter and number appearing in parenthesis after the chemical name denote the code number assigned to each polymer. The abbreviations for solvents denote the following: MEK is methyl ethyl ketone, TOL is toluene, DMF is dimethylformamide, MA is methyl alcohol, B is benzene, and EA is ethyl acetate.

[2]The following symbols denote the curing time and temperature and bonding pressure employed in making the bonded metal specimens:

A   is 60 minutes at 320° F and 50 pounds per square inch bonding pressure.
A-1 is 60 minutes at 320° F and 250 pounds per square inch bonding pressure.
B   is 30 minutes at 400° F and 200 pounds per square inch bonding pressure.
B-1 is 30 minutes at 400° F and 50 pounds per square inch bonding pressure.
C   is 16 hours at 400° F at contact pressure (heated in oven).
D   is 60 minutes at 350° F and 250 pounds per square inch bonding pressure.
E   is 16 hours at 450° F at contact pressure (heated in oven).

[3]Specimens were aged for 100 hours at the elevated temperature and then cooled and tested at 80° F.

[4]Shear strength in pounds per square inch. Average of tests on 5 or more specimens.

[5]Percent of bond area failing in adhesion to the metal surface. Average of tests on 5 or more specimens.

[6]Percent of bond area showing char or discoloration. Each value is the average of tests on 5 or more specimens.
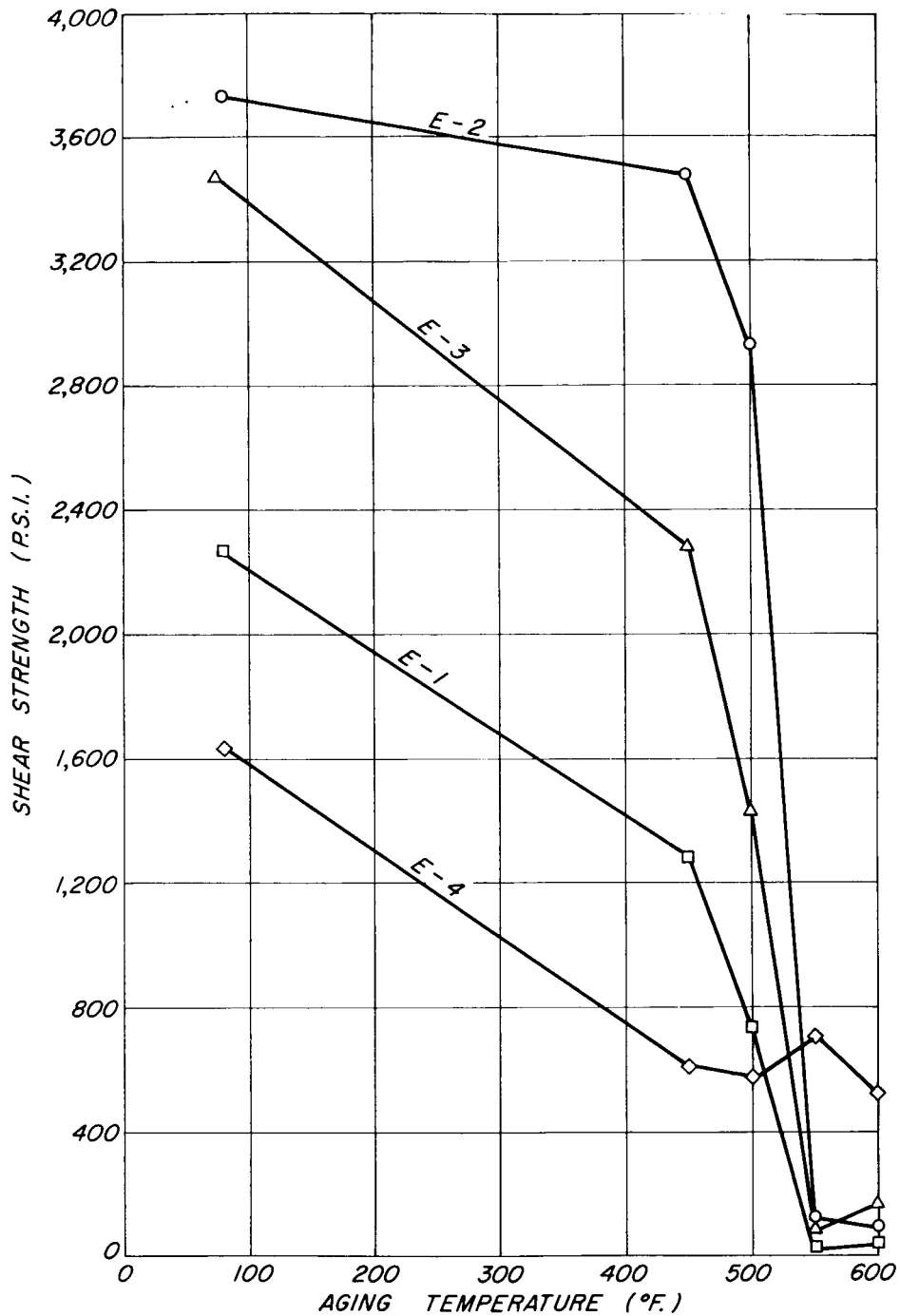
Figure 1.- Shear strength of bonds to aluminum made with various epoxy
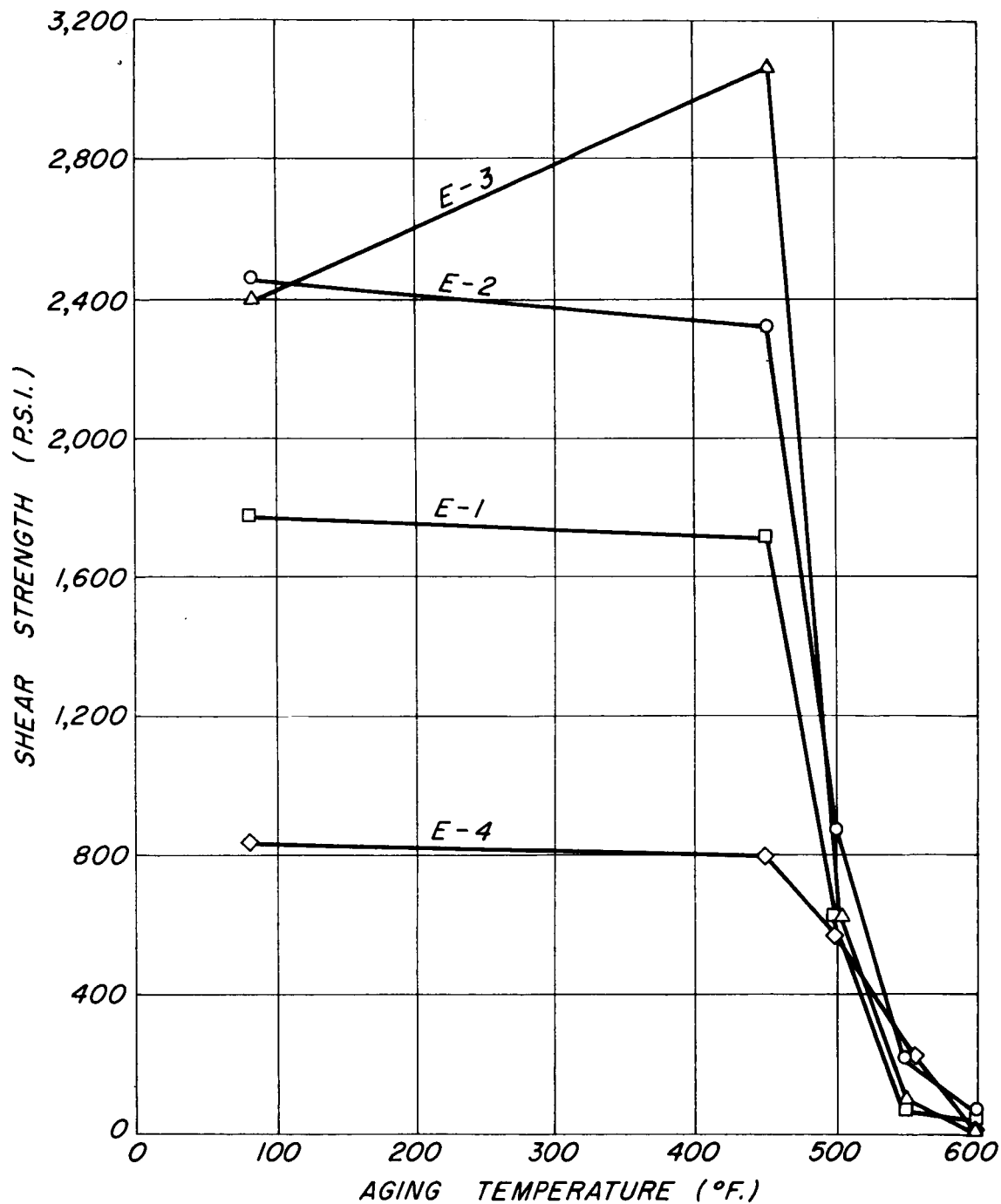resins and tested at 80° F after aging 100 hours at several different
temperatures.

Figure 2.- Shear strength of bonds to stainless steel made with various epoxy resins and tested at room temperature after aging 100 hours at several different temperatures.